EVALUATION OF THE POTENTIAL IMPACT OF CONTAMINANTS ON AQUATIC RESOURCES IN THE CENTRAL VALLEY AND SACRAMENTO-SAN JOAQUIN DELTA ESTUARY

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Population levels of aquatic organisms in the Sacramento-San Joaquin Delta Estuary are in decline (Herbold *et al.*, 1992). The purpose of this review is to evaluate the potential contribution of toxics in the collapse of these resources. Possible impacts of pesticides and metals are assessed[1]. Pesticide impacts are emphasized as work done to date suggests that these may pose the greatest threat to aquatic organisms in the Central Valley and Delta. Finally, suggestions for possible follow-up work are included to help fill gaps and clarify potential impacts.

The CALFED Bay-Delta Program has requested that the University of California prepare a document reviewing contaminant impacts on aquatic organisms in the Sacramento-San Joaquin Delta Estuary (Bailey, in prep). The University review primarily covers the impact of contaminants on aquatic resources in the Estuary while the present document emphasizes impacts in the Valley.

PESTICIDES

It is important to emphasize that Regional Board staff are unaware of any data which suggest that the level of pesticides now being detected in surface water pose a human health threat. Also, there is little evidence that suggests that chemicals are being used illegally. Rather, the data suggest that the recommended application instructions for some pesticides are inadequate to protect aquatic life.

Most of what is known about the potential impact of pesticides on aquatic organisms in the Central Valley come from studies employing the EPA three species bioassay protocol (EPA, 1985;1989). The Central Valley Regional Water Board has conducted two major bioassay studies, one in the Sacramento and the other in the San Joaquin watershed and follow-up work to better understand the significance of the initial findings. Overall, our understanding of pesticides in surface water is still very limited. However, the results suggest widespread occurrence of a few insecticides at levels that may impact the invertebrate portion of the aquatic food chain in both the Valley and Delta. More limited data exist which suggests possible impacts on primary producers and fish. Follow-up work by both the Department of Pesticide Regulation and the U.S. Geological Survey are cited which confirm the presence of the pesticides.

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[1]Other chemicals of concern--PCBs, PAHs, and dioxins/furans--which are elevated in some fish in the Estuary (San Franciscso Regional Water Quality Control Board, 1994) are not covered although they may pose toxicological impacts on top predator species. Likewise, potential sediment toxicity is not evaluated although reported for San Francisco Bay (SFEI, 1994).

Sacramento Valley

The Sacramento Valley bioassay study was conducted between 1987-90 and emphasized the toxicity of rice return water in April and May (Foe and Connor, 1991a). Acute[2] *Ceriodaphnia* mortality, the invertebrate component of the EPA three species bioassay, was observed each year in water from Colusa Basin Drain. In 1989 toxicity was traced as far downstream on the Sacramento River as the City of Rio Vista (the most seaward sampling site). Toxicity identification evaluations[3] (TIES) with *Ceriodaphnia* implicated methyl parathion, carbofuran and malathion as the cause of mortality (Norberg-King *et al.*, 1991). The Central Valley Regional Water Quality Control Board amended its Basin Plan to include rice insecticide performance goals. These required the progressive reduction of insecticide concentrations in surface water. Monitoring has since demonstrated that the resulting changes in rice cultivation have largely corrected the insecticide problem in the Sacramento River (Schnagl, 1994).

The impact of pesticides on indigenous aquatic organisms has only been evaluated in the case of rice return water. Discharge from Colusa Basin drain was found to be acutely toxic to both striped bass larvae and *Neomysis mercedis* (Bailey *et al.*, 1994). Rice return water was consistently more toxic to *Neomysis,* the local invertebrate tested, than to *Ceriodaphnia*, the EPA three species bioassay organism (Foe and Connor, 1991a). Follow-up work by the Department of Fish and Game established that methyl parathion was the primary insecticide responsible for *Neomysis* toxicity (Finlayson *et al.*, 1993). A strong correlation was noted between the decrease in larval striped bass recruitment in the Sacramento River and the pounds of rice pesticide applied in the Basin divided by the River's flow rate (Foe and Connor, 1991a; Bailey *et al.*, 1994). Further support for probable rice impacts on local bass populations come from histopathological studies by Bennett *et al.* (1995). Liver abnormalities were observed in 26-30 percent of all larval bass caught downstream of Colusa Basin drain in the Sacramento River between 1988 and 1990. The porportion dropped to 15 percent in 1991. The histopathological abnormalities were consistent with toxic exposure.

San Joaquin Valley

A two and a half year bioassay study was conducted between 1988-90 to assess the quality of all the major types of water moving through the San Joaquin Basin (Foe and Connor, 1991b). The principal conclusion of the study was that there was a 43 mile reach of the San Joaquin River between the confluence of the Merced and Stanislaus which tested toxic about half of the time to *Ceriodaphnia*. Toxicity appeared to be caused by pesticides carried in storm and

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[2]Death within 96 hours.

[3]TIES are a series of physical and chemical manipulations conducted in conjunction with toxicity tests to identify the agent(s) responsible for toxicity (U.S. EPA 1991a; 1993a,b; Bailey, et al., 1995).

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irrigation tailwater runoff from row and orchard crops. Orestimba Creek and Turlock Irrigation District Lateral Number 5 were monitored as representative of west and eastside agricultural inputs. The two sites tested toxic 42 and 75 percent of the time to *Ceriodaphnia*, respectively. Limited chemical monitoring was done, however, on five occasions diazinon, carbofuran, parathion and carbaryl were detected in these drains and the San Joaquin River at concentrations in excess of recommended criteria to protect freshwater aquatic life and of concentrations reported to be toxic to sensitive invertebrates including *Ceriodaphnia.*

Follow-up studies by the Regional Board and the U.S. Geological Survey attempted to better define the pesticides causing toxicity in the San Joaquin Basin, the responsible agricultural practices and pesticide fate in the aquatic environment. Study results fall naturally into wet and dry weather events.

Wet weather--Orchards In January and February about a million pounds of diazinon, chlorpyrifos, malathion, and methidation are applied in the Central Valley on about half a million acres of stonefruit for the control of boring insects (Department of Pesticide Regulation, 1990;Foe and Sheipline, 1993). The only major use of the chemicals then is on orchards. All four chemicals have been detected in surface water (Foe and Sheipline, 1993; Foe, 1995). However, diazinon appears to pose the greatest threat to aquatic organisms as it was regularly present with the greatest number of toxic units[4]. Foe and Sheipline (1993) conducted a study in 1992 to ascertain whether dormant spray problems were restricted to the San Joaquin or occurred wherever there are orchards. The study found diazinon in about half of all small water courses surveyed during dry periods. All drainages became toxic after a large storm. The San Joaquin River at Vernalis had acutely toxic concentrations of diazinon (to *Ceriodaphnia)* for 8 days after the largest storm of the year. Kuivila and Foe (1995) followed up on these observations in the winter of 1993 and attempted to measure dormant spray insecticides in both the Sacramento and San Joaquin Rivers after rainstorms. Elevated concentrations of diazinon were observed in both Rivers after the two largest rainfall events of the year. During the first storm, the San Joaquin River at Vernalis contained acutely lethal concentrations of diazinon to *Ceriodaphnia* for 12 days. On the second occasion, diazinon levels in the Sacramento River were sufficiently high at Rio Vista to kill test organisms for three consecutive days and were subsequently traced at these concentrations as far seaward in the Estuary as Chipps Island. The Department of Pesticide Regulation has confirmed the presence of diazinon in stormwater in the San Joaquin River in January 1992 and February 1993 and in the Sacramento River in February 1994 (Ross, 1992a;1993a; personal communication, Nordmark). In conclusion, the annual contamination of Central Valley and Delta waterways by orchard dormant sprays at lethal concentrations to sensitive organisms appears to be a regular event.

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[4]Ambient chemical concentration/concentration killing 50 percent of test organisms in laboratory water in 96 hours.

Alfalfa In March and April about a million pounds of diazinon, chlorpyrifos and carbofuran are applied in the Central Valley on alfalfa for weevil control (Department of Pesticide Regulation, 1990; Foe and Sheipline, 1993). In 1991 the U.S. Geological Survey began daily monitoring of the San Joaquin River at Vernalis for pesticides (Crepeau *et al.*, 1991). A well defined carbofuran and diazinon peak and traces of chlorpyrifos were detected coincident with heavy rains in early March from applications on alfalfa. Simultaneously, the Geological Survey conducted a study to assess the concentration and distribution of alfalfa pesticides in the Sacramento-San Joaquin Delta Estuary (Kuivila *et al.,* 1992). Carbofuran, but not diazinon, increased westward in the Estuary to Chipps Island. The increase in carbofuran was attributed to inputs from local unmeasured alfalfa sources within the Delta while the decrease in diazinon was thought to result from dilution with uncontaminated seawater. The next year Foe and Sheipline (1993) attempted to confirm Kuivila's results and determine whether carbofuran would reappear in the Estuary. The spring of 1992 was unusually dry and little toxicity from alfalfa applications was observed. The U.S. Geological Survey also saw no diazinon, chlorpyrifos or carbofuran in surface water in the spring of 1992 (MacCoy *et al.*, 1995). However, March 1995 was very wet. Chlorpyrifos, and carbofuran were observed, consistent with applications on alfalfa, in small upland waterways and in delta back sloughs at concentrations acutely toxic to *Ceriodaphnia* (personal communication, Bailey) Finally, the Department of Pesticide Regulation confirmed the presence of diazinon and carbofuran in small water courses and in the San Joaquin River in March and April of 1991 and 1992 (Ross, 1991 and 1993b). Chlorpyrifos was only measured in 1991. In conclusion, application of alfalfa insecticides probably pose a threat to sensitive aquatic invertebrates in small Central Valley water courses each year while organisms in the rivers and Delta are only at risk during wet springs.

Urban runoff Last year Regional Board staff began a multi-year study to identify the constituents in urban storm runoff responsible for toxicity to each of the EPA three species bioassay organisms. The most significant finding was the ubiquitous lethality of diazinon to *Ceriodaphnia* in runoff from many Bay area and Central Valley cities including Stockton whose runoff drains into back sloughs in the eastern Delta (Connor 1994, 1995a, 1995b). For *Ceriodaphnia,* additional constituents of concern include chlorpyrifos, malathion, copper, zinc and nickel (Connor 1995a). TIEs with *Selenastrum*, the algal component of the EPA three species bioassay, have identified the herbicide, diuron, and copper and zinc as causing toxicity (Connor 1995a;1995c). Finally, runoff from the first major storm of the year in Stockton appears to annually produce an oxygen deficit causing fish kills in adjacent Delta back sloughs. The cause of the deficit is not yet known.

The widespread occurrence of diazinon in urban creeks prompted a follow up study to determine the source(s). Both diazinon and chlorpyrifos have been detected simultaneously in city creeks and in composite rainfall samples in a pattern that suggests the pesticides are coming from both urban and rural sources. The pesticides are found in urban creeks throughout the year, but concentrations peak during the orchard dormant spray season. At this time high levels of pesticides were detected in rain samples collected as far apart as the cities of Patterson and Red Bluff (Connor, in prep). The highest concentrations of diazinon were measured near orchards. Diazinon values in some rain samples exceeded the *Ceriodaphnia* 96 hour LC_{50} concentration[5] by over an order of magnitude. Pesticides have previously been reported in both fog and composite rainfall samples from the San Joaquin and Tulare basins (Glotfelty *et al.*, 1987, 1990; Oltmann and Shulters, 1987); however, these are the first data for the Sacramento Valley and many of the values appear higher than reported elsewhere.

San Joaquin Valley--Dry weather *Ceriodaphnia* lethality was also observed in the San Joaquin River bioassay study during the spring and early summer (Foe and Connor, 1991b). Subsequent investigations were initiated to determine the cause of toxicity. Thirty-eight percent of all agricultural return water samples collected in the Basin between April and June of 1991 and 92 were acutely toxic (Foe, 1995a). In both years the last precipitation fell by mid-April. Therefore, most of the water tested was irrigation return flow with tailwater[6] believed to be the primary vehicle transporting pesticides from fields into surface water. Diazinon, chloryprifos, fonofos and carbaryl were detected in surface water at acutely toxic concentrations to *Ceriodaphnia*. The four chemicals are widely used in agriculture in the late spring so it is difficult to precisely determine the crops from which they originate. Chlorpyrifos is predominately used at this time on walnuts, almonds, apples and corn; diazinon on melons, tomatoes and apricots; fonofos and carbaryl on beans and tomatoes. Monitoring by the Department of Pesticide Regulation and the U.S. Geological Survey has confirmed the presence of diazinon, chlorpyrifos and carbaryl in surface water in the Basin at this time (Ross, 1991,1993c, MacCoy *et al.*, 1995). Fonofos was not detected.

Another bioassay study is being conducted in the Delta (Deanovic, in prep; Bailey, personal communication). Acute *Ceriodaphnia* mortality has been observed in water samples collected from upland agriculturally dominated creeks and constructed drains discharging to the Delta and in Delta back sloughs. Diazinon, chlorpyrifos and carbofuran were measured in these samples at concentrations known to kill *Ceriodaphnia*. Again, the primary source of the chemicals is believed to be irrigation tailwater from upland row and orchard crops.

To date no studies have ascertained whether tailwater from row and orchard crops in the Sacramento Valley are also contaminated with pesticides. However, the same agricultural practices are employed and frequent non rice related toxicity observed (Connor *et al.*, 1995) so it is possible that pesticide contamination from tailwater runoff will also be found.

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[5]Concentration that kills half of all test organisms in laboratory water in 96 hours.

[6]Water from irrigated orchard, row and field crops.

Finally, periodic toxicity to *Selenatrum* has been observed in the Sacramento and San Joaquin Rivers and Delta (Connor *et al.*,1995; Foe and Connor, 1991b; personal communication, Bailey). Toxicity appears to occur during both wet and dry periods. Recently, U.C. Davis has begun conducting algal TIES in Delta water and discovered that *Selenastrum* production can often be improved by passing water samples through a C8 cartridge, suggesting phytotoxicity from organic(s). Simazine and diuron were measured in some of these samples at concentrations known to be toxic to *Selenastrum*. However, the data also suggest the presence of other unidentified contaminants. In addition, the U.S. Geological Survey has identified a number of pesticides, including herbicides and fungicides, in water samples collected from the Sacramento and San Joaquin Rivers and Delta (MacCoy *et al.*, 1995;Kuivila, personal communication). Insufficient information is available in the literature to evaluate their toxicological significance to either *Selenastrum* or local primary producers.

METALS

Most metals in the Central Valley watershed originate from mine wastes located in the Sierra Nevada, Cascade and Coast range mountains and, with the exception of Iron Mountain Mine, collect in foothill reservoirs before discharge downstream. A two year study of total recoverable and dissolved metals[7] in releases from Central Valley Reservoirs using clean collection techniques demonstrates that exceedances of water quality objectives were primarily detected downstream of Keswick Reservoir (Connor and Deanovic, in prep). Concurrent toxicity testing with the EPA three species was conducted. Toxicity was primarily limited to *Selenastrum* in River reaches downstream from Keswick Reservoir. Algal toxicity was linked to dissolved copper and zinc. The downstream extent of *Selenastrum* toxicity was not ascertained. However, metal toxicity did not extend to the Delta as the Sacramento River at Hood never tested toxic.

Bimonthly measurements of metals[8] were taken between September 1991 and August 1993 from the Sacramento River below the City of Sacramento (Walker and Associates, 1993). The data demonstrate periodic exceedances of the EPA recommended total recoverable criteria for copper, lead and mercury and dissolved criteria for lead and mercury. These values appear comparable, with the exception of mercury, to a much smaller data set collected by Regional Board staff in 1993-94 (Foe in prep). Some caution must be exercised in interpreting all the metal information as it was collected during drought years. Metal concentrations in the upper River are known to have decreased (personal communication,

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[7]Copper, cadmium, zinc, nickel, lead, chromium, arsenic, silver and iron.

[8]Arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, and zinc were collected and analyzed with clean techniques.

Heiman). It is not known whether this decrease is the result of the drought changing the dynamics of metal releases in the upper watershed or of Regional Board mine discharge abatement activities. If the drought is the primary cause of the decrease, then exceedances of water quality objectives may increase and possible metal toxicity occur with a return to more normal precipitation patterns.

The Regional Board has, as part of the ongoing Bay Protection Toxic Cleanup program, a metal monitoring element with three objectives: (1) To define the extent of metal objective exceedances throughout the Delta; (2) To define the extent of metal associated toxicity throughout the Delta; and (3) to determine the metal loading patterns to the Delta, with an emphasis on storm events. Two patterns have emerged after almost two years of study: no incidents of toxicity have been linked to metals and exceedances of water quality objectives appear to generally be limited to storm events. Again, whether these patterns will remain with changes in precipitation are not known.

The San Francisco Bay Regional Board has recently adopted a copper water quality objective and report periodic exceedances in San Francisco Bay (SFEI, 1994). The Board has determined that riverine discharges from the Central Valley are responsible for over half the copper load (Lacy, 1993). While background copper concentrations are elevated in the Bay, evidence of toxicological impacts are lacking (San Francisco Bay Regional Water Quality Control Board, 1992).

A mercury health advisory has been issued for the Estuary recommending a restricted consumption of striped bass. Recent monitoring in the Bay demonstrate that other edible fish also have elevated tissue mercury concentrations (San Francisco Regional Water Quality Control Board, 1994) Riverine inputs are the principal source of the element (Gunther *et al.*, 1987). Monitoring of the lower Sacramento River in 1993-94 during low flow conditions (8,000-12,000 cfs) with clean metal techniques demonstrated that total recoverable mercury concentrations averaged 2-4 ng/l (Foe,1995b) but see Walker and Associates (1993) for higher values. The Regional Board data are well below the U.S. EPA recommended freshwater criteria of 12 ng/l. The criteria was established to protect human health. Monitoring data for San Francisco Bay also demonstrate that background mercury levels were below recommended criteria during 1993 (SFEI, 1994). However, periodic exceedances were noted in Pacheco Creek, the Napa River and Grizzly and San Pablo Bays.

Past riverine monitoring has indicated that the principal loading of metals to the estuary occurs during periods of high flow. The winter of 1995 was very wet. Beginning in January metal samples were collected daily by Regional Board staff during peak flows and twice weekly thereafter from the Sacramento River below the City of Sacramento (Greene's Landing) and from the Yolo Bypass at Prospect Slough. Preliminary results are only available for mercury. Mercury concentrations in the Sacramento River and Prospect Slough ranged for several months between 10-85 and 15-700 ng/l, respectively. The high concentrations in Prospect Slough suggested a possible local source. Follow-up studies determined that Cache Creek was discharging mercury into the Bypass at concentrations between 400-2200 ng/l. Preliminary load estimates suggest that the Creek[9] may be a major source of estuarine mercury.

ECOLOGICAL SIGNIFICANCE OF CONTAMINANT FINDINGS

PESTICIDES The ecological significance of elevated pesticide levels in the Central Valley is not known. However, indirect evidence suggests that impacts may be occurring to sensitive aquatic organisms in both the Valley and the Sacramento-San Joaquin Delta Estuary.

Direct evidence of ecological impacts on aquatic communities is notoriously difficult to measure (Clements and Kiffney, 1994; DeVlaming, 1995). The U.S. EPA developed the three species bioassay approach (EPA, 1985;1989) as an early warning system to help others detect pollutant impacts in freshwater. The Agency attempted to validate the approach by conducting eight freshwater studies to ascertain whether there was a correlation between toxicity in receiving water as measured by their tests and instream impacts (reviewed in U.S. EPA, 1991b). The bioassay results predicted receiving water impacts at seven sites. At each location differences were measured in the abundance and distribution of aquatic organisms below the site as compared to above it. At one location no difference was predicted by the bioassay testing and none was detected in the receiving water. Subsequent work by Eagleston *et al.*, (1990), Birge *et al* (1990) and Dickson *et al.* (1989) provide further support for the hypothesis that bioassays can be an indirect method of assessing whether pollutants are impacting freshwater organisms. These results have lead the U.S. EPA to recommend bioassay testing as an acceptable surrogate to the measurement of the abundance and distribution of organisms at sites where impacts from pollutants are suspected. However, the method has been criticized by Marcus and McDonald (1992) and Parkhurst (1995). Recently, DeVlaming (1995) reviewed all the studies and has concluded that there is a good qualitative relationship between bioassay results and aquatic ecosystem responses. The relationship appears particularly robust if acute toxicity is observed in the bioassays.

Concentrations of diazinon in the Central Valley, reported toxicity of the chemical to aquatic organisms and recommended criteria to protect aquatic life are summarized below to help illustrate the potential aquatic threat posed by insecticides. Diazinon was selected for analysis as it is a common pesticide for which much high quality data exists. However, the concentrations, distribution and toxicity patterns of the chemical are not unique. One quarter to over half of all samples collected in studies in the Central Valley contained measureable

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[9]Creek flows are estimated to have been in excess of a million acre-feet during the winter and early spring of 1995.

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concentrations of diazinon (Table 1). The frequency of detections are higher in bioassay (Foe and Connor, 1991b; Foe and Sheipline, 1993; Foe, 1995a) than in routine pesticide surveillance work (MacCoy *et al.*, 1995; Ross, 91;92a,b;93a,b,c). This is because the bioassay studies screened large numbers of samples and only analyzed ones testing toxic for pesticides while the routine monitoring studies randomly selected samples for analysis. As a result, the latter studies provide the best information about ambient diazinon concentrations in the watershed.

Analysis of toxicity data demonstrate that fish are more tolerant of diazinon than invertebrates (Table 2). Among invertebrates, *Daphnia magna* and *Gammarus faciatus* are about twice as sensitive as *Ceriodaphnia*. Little chronic toxicity information is available for fish or invertebrates. In such situations, EPA (1991b) recommends that safe concentrations be estimated by calculating acute to chronic ratios[10] (ACR) for different classes of organisms and multiplying the ACR and acute data together to estimate safe levels. ACRs for invertebrates (*Mysidopsis* and *Ceriodaphnia*) and for fish (fathead minnow) are about 4 and 70, respectively. Therefore, safe concentrations for the most sensitive invertebrates and fish listed in Table 2 are assumed to be below 0.05-0.10 and 0.2-2.0 ppb, respectively. The diazinon data in Table 1 suggest that for fish, no acute and little to no chronic toxicity should exist in Central Valley water. In contrast, for sensitive invertebrates, 1 to 10 percent of the time the water should be acutely lethal and 10 to 30 percent of the time chronically toxic.

Recommended diazinon criteria to protect freshwater aquatic life are summarized in Table 3. The International Joint Great Lakes Commission (1975) and the National Academy of Sciences (1973) have published recommend maximum criteria for diazinon of 0.008 and 0.009 ppb, respectively. Both values are at or below the detection limit of all the pesticide analytical studies conducted in the Central Valley. Therefore, all detections are at or above these criteria. The two criteria were exceeded, at a minimum, 25 to 50 percent of the time (Table 1). The California Department of Fish and Game has published a chronic criteria of 0.04 ppb (Menconi and Cox, 1994). The Department recommends that freshwater organisms should not be unduly affected by diazinon if the four day average concentration does not exceed 0.04 ppb more often than once every three years. Pesticide monitoring demonstrates that the Fish and Game criteria is being exceeded between 11 and 32 percent of the time (Table 1).

An analysis of fifteen years of Department of Fish and Game zooplankton tow data has recently been completed (Obrebski *et al.*, 1992). The study demonstrates a decline in abundance of zooplankton species (copepods, rotifers and cladocerans) in the freshwater portion of the Estuary. In contrast, population levels of species inhabiting intermediate and marine salinities have largely remained stable. The cause of the decline of freshwater forms

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[10]LC_{50} concentration/NOEC concentration.

is not known. However, these are the most sensitive species to insecticides (Sheipline, 1995). Historically, it seems likely that a portion of the freshwater zooplankton community in the Delta was the result of a continuous repopulation with individuals from slow moving, warm, eutrophic waters in the Valley. The repopulation is probably most important for the Rivers with their strong downstream flows. The primary nursery areas in the Valley are likely to have included the agriculturally dominated creeks and constructed drains which now contain pesticides at toxic concentrations to many zooplankton.

An alternate, but not mutually exclusive, explanation for some of the decline in zooplankton abundance is that phytoplankton production in the watershed is being suppressed by elevated metal and herbicide concentrations. Primary production in the estuary has declined by an order of magnitude (Alpine and Cloern, 1992). The abundance of at least one zooplankter, *Neomysis*, is positively correlated with chlorophyll a concentration suggesting food limitation (Orsi and Mecum, 1994). *Selenastrum* TIEs demonstrate copper and zinc phytotoxicity in the upper Sacramento River and organic inhibition, including diuron and simizine impacts, in the San Joaquin River and Delta. The data also suggest the presence of other unidentified contaminants. Little is known about the concentration and distribution of any of these, although the U.S. Geological Survey reports an almost ubiquitous distribution of simazine throughout the watershed (MacCoy *et al.*, 1995).

Zooplankton are important in aquatic systems, in part, as food for larval and juvenile fish. Zooplankton densities in the freshwater portion of the Estuary are now reported to be one to two orders of magnitude lower than in the early seventies (Obrebski *et al.*, 1992). The population of many freshwater fish in the Estuary are also in decline, including species like splittail, delta smelt and striped bass whose larvae feed almost exclusively on small zooplankton. Laboratory evidence suggests that food levels in the Estuary are limiting, at least for striped bass larvae (reviewed in Herbold *et al.*, 1992). However, no evidence of field starvation (death from lack of food) has been found although increased larval predation rates are hypothesized because of suppression in growth from both toxics and lack of food (Bennett *et al.*, 1995).

Metals Metals periodically exceed water quality objectives and undoubtedly cause toxicity in some watercourses above major reservoirs (Montoya and Pan, 1992). However, the only evidence of metal impacts below the mines are toxicity to *Selenastrum* in the upper Sacramento River and in urban runoff and toxicity to many forms in the controlled spills from Iron Mountain Mine (NOAA, 1989). Control of acid mine drainage at Iron Mountain Mine is now being evaluated as part of the U.S. EPA superfund program. Possible ecological impacts of metal phytotoxicity was previously discussed in conjunction with potential zooplankton food limitation. This is believed, unless metal concentrations rise with increased precipitation, to be the major potential ecological impact of suspended metals on aquatic biota in the watershed. Potential metal and pesticide phytotoxicity should be evaluated jointly.

Mercury biomagnifies in aquatic ecosystems and at high tissue concentrations can become a potent neurotoxin. No evidence of mercury impacts on biota are known for the Delta or Estuary. However, to our knowledge few studies have looked for impacts in top predator birds, fish or mammals. Present concern about elevated mercury concentrations in fish tissue arise because of possible human health effects.

Historically, mercury was mined in the coastal range and transported across the Valley for use in Placer gold mining in the Sierra Nevada mountains. A number of abandoned mercury mines are known in the Cache and Putah Creek watersheds (Montoya and Pan, 1992). However, the coastal range mines have not been evaluated for their potential to contribute mercury to the Estuary because during most years their runoff does not reach the system. No thought was given to evaluating impacts during wet weather. Follow-up studies evaluating the feasibility of mercury abatement projects in the Cache Creek watershed are recommended as they may prove to be a cost effective way of reducing estuarine mercury contamination.

SUGGESTED FUTURE WORK

Follow-up monitoring in the Central Valley should emphasize the collection of information in four general areas: continuation of present bioassay-chemical testing, evaluation of the ecological significance of the present contaminant findings, development of information determining primary factors responsible for controlling the movement of pesticides from agriculture into surface water and conducting a detailed reconnaissance survey of the Cache Creek watershed to determine whether successful mercury abatement projects are possible. The rationale and objectives for each area of work are discussed below. Detailed study plans can be developed if interest and resources become available.

I. Bioassay-chemical monitoring It is recommended that EPA three species bioassays and associated TIEs be continued in both the Sacramento and San Joaquin watersheds and in the Delta to attempt to identify all the primary contaminants, their sources and the likely extent both temporally and spatially of aquatic impacts. The work should not be limited to agricultural areas but also include evaluation of water quality from the major dams and from urban areas. In addition, more chemical monitoring needs to be conducted in the Delta to establish ambient pesticide concentrations in back sloughs from local agricultural inputs. There are three main reasons why additional bioassay-chemical monitoring is recommended.

First, all early bioassay studies in both the Sacramento and San Joaquin Valleys were collected without accompanying TIEs and, in most cases, with minimal chemical monitoring. (Foe and Connor, 1991b; Connor *et al.*, 1995; Foe and Sheipline, 1993; Foe, 1995a). As a result, the successful identification of responsible toxic agent(s) was highly variable. Chemicals causing toxicity were not identified about half of the time, in spite of occasional widespread evidence of impairments. More success is likely in the future with the regular use of TIEs. TIEs procedures have been developed for the fish and invertebrate component of the

EPA three species (EPA, 1991a,1993a,b; Bailey *et al.* 1995). Algal TIE procedures are under development and some of the field results look very promising. Recently, U.C. Davis has begun to routinely conduct *Ceriodaphnia* TIEs with toxic water samples from the Delta and have been very successful in identifying the primary chemicals responsible for acute toxicity (personal communication, Bailey). Similar success is likely elsewhere if the same procedures are used. Identification of all the principal contaminants causing toxicity to the EPA three species is essential for understanding the contribution of toxics in the regulation of the abundance and distribution of local organisms and for the development of a comprehensive contaminant regulation program.

Second, all bioassay work conducted to date has occurred during drought conditions (1988-94). Water availability may be very important both in driving contaminants off site during wet periods and in providing dilution once in the receiving water. Our present understanding of pesticide and metal dynamics in the Central Valley are inadequate to enable us to predict whether changes in water year types should improve or excascerbate contaminant problems. Therefore, continued monitoring in other water year types is essential to complete our understanding of contaminant impacts.

Finally, only about two years of bioassay monitoring has been done in the Delta. All fish and most algal testing was discontinued after the first year because of lack of money. We believe that several more years of monitoring with all three species is warranted because of the importance and complexity of the Delta. In addition, little chemical monitoring has been conducted in the Delta to determine *in situ* pesticide concentrations. In a number of cases, bioassay monitoring in back sloughs have identified lethal concentrations of pesticide which could only have come from local inputs. Future chemical monitoring should emphasize the collection of ambient pesticide data in representative backslough areas with inadequate flushing to provide better information on the chemicals being discharged and their concentration range.

II. <u>Ecological impacts</u> Aquatic biological resources in the Sacramento San Joaquin Delta are in decline. Many factors have been advanced to explain the collapse including water diversions, changes in basin hydrology, loss of habitat, introduction of exotic species and toxics. All of the above probably contribute to the decline, with the amount varying both by year and species. However, to date few attempts have been made to estimate and rank the relative importance of any of these factors. This information is essential, although difficult to obtain, because future efforts must concentrate on correcting the most serious problems first. It is believed that an overall sense of the relative importance of toxics can be gained from an incisive combination of laboratory and field work. Some possible experiments are summarized below by trophic level.

Phytoplankton The primary problem with our present algal bioassay data is that it is not known how the sensitivity of *Selenastrum* compares with that of local species. *In situ* bioassays with indigenous phytoplankton should be conducted seasonally in both Delta and Central Valley water to ascertain this. The testing should consist of amending enviromentally realistic concentration gradients of pesticide and/or metals into representative local water which had previously been filtered to remove herbivorous zooplankton and comparing the resulting production rates in amended and unmanipulated treatments. Test endpoints should include both alterations in primary production rates and changes in algal species composition. If phytotoxicity with local organisms is observed, then impacts on ambient primary production rates can be estimated by combining information on the temporal and spatial distribution of the contaminant(s) with the amount of algal suppression observed in the bioassays. Finally, the relative importance of phytotoxicity and water diversions can be roughly estimated for specific waterbodies by comparing the above values with calculated changes in production assuming that phytoplankton are cropped at a rate porportional to the fraction of the total available water pumped. If phytotoxicity is found to be widespread, then changes in primary production can be compared with estimates of the loss in productivity by diverting water at the State and Federal pumping facility (Jassby and Powell, 1994).

Zooplankton Evaluating the ecological impact of insecticides is difficult as little toxicity data exists for many local species. In addition, much of the available information is for relatively short term exposure (several days to about a quarter of an organisms life span) and for constant pesticide concentrations. The actual dynamics of pesticide exposure in the Central Valley and Delta are unknown; however, they are unlikely to be of this nature. More realistic are either long-term, low level exposure (> half an organisms life span) or repeated short-term exposure (one to several day) to different chemicals at high concentration followed by long-term, low level exposure. Little toxicity information exists in the literature comparing these exposure regimes to the traditional static renewal constant concentration type of bioassay presently conducted (Clark *et al.*, 1993). Therefore, realistic assessments of the ecological impact of pesticides in the Sacramento-San Joaquin watershed require both the development of bioassays for local species and more information about pesticide fate. Once developed, information in both areas can be combined to produce a more realistic assessment of potential toxicological impacts. Needs in both of the above fields are discussed more fully below.

To be valid, laboratory exposures should attempt to mimic, as closely as possible, actual instream pesticide concentration patterns, their duration and frequency of reoccurrence. Some pesticide concentration and frequency data are available for Central Valley drainages and the Delta. However, less is known about the duration and subsequent decrease in pesticide concentrations over time. Dissipation rates are primarily a function of the duration of the initial input, a chemical's degradation rate and available hydrologic dilution. Most pesticide inputs observed to date in large waterbodies seem to be of short duration (1-10 days). Individual chemical degradation rates are available from the literature. However, low temperature studies (10^0C) in local water by the U.S. Geological Survey suggest a much

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longer half life than generally reported in the literature (Kuivila and Crepeau, 1995). More work is needed in Central Valley water at higher temperatures (20-25^{0}C) to better estimate summer degradation rates. This information can be compared with hydrologic estimates of available dilution and flushing to determine actual pesticide concentrations over time.

Simultaneously, long-term flow-through bioassay protocols should be developed for important, sensitive local species. Such protocols already exist for *Neomysis mercedis* (ASTM, 1992). Other candidate organisms might include a rotifer, *Eurytemora affinis*, and a benthic amphipod such as *Corophium* sp. Bioassay endpoints should include mortality, alterations in time to first reproduction and total reproductive output. Once developed, bioassays should be conducted using realistic estimates of insecticide exposure to determine probable biological impacts. The resulting information can be used to estimate the relative ecological impact of pesticides and water diversions in individual waterbodies. Insecticide impacts can be estimated by fitting the demographic changes observed in the bioassays into population models to predict long term changes in population structure and density. Similarly, impacts from water diversions can be estimated by assuming that small zooplankton species possess no avoidance mechanisms and are diverted at a rate porportional to the fraction of total available water pumped.

Fish Pesticide levels do not appear sufficiently high to cause measurable impacts on Fathead minnow larvae using the EPA three species bioassay protocol. Short-term bioassays with local species are unlikely to produce different results. If fishery impacts are occurring, they are likely to be more subtle and require different techiques to measure. Two possible impacts are decreased larval growth either by producing histopathological abnormalities or by decreasing available food. Either endpoint should result in reduced adult recruitment by prolonging the amount of time spent as a small fish subject to a high predation rate (Bennett *et al.*, 1995).

Bennett (1995) has proposed evaluating archieved Delta smelt larvae from good and bad recruitment years for histopathological abnormalities induced by exposure to toxins and suppressions in growth which could result from either pollution exposure or lack of food. Growth rates would be estimated from otolith analysis while histopathology assessments would be conducted by methods similar to Bennett *et al.* (1995). I believe the proposed study is an excellent initial attempt to discern sublethal impacts with larval Delta Smelt. However, from an ecosystem perspective, the study would be strengthened if other species could also be examined. Possible additional candidates are splittail and striped bass from the Delta and threadfin shad from the Valley.

III. Determination of the primary factors responsible for controlling off target movement of pesticides from agriculture Best management practices must be developed to insure that pesticides can continue to be used in California without posing an aquatic threat to local populations. A necessary first step is to determine the primary factors responsible for controlling the off target movement of pesticides from urban and agricultural areas and their relative importance. This work is essential to focus the future development of best management practices on the most important variables first. Some potential mechanisms inducing off-target pesticide movement in winter from orchard and alfalfa fields are reviewed in Foe and Sheipline (1992) while factors influencing summer tailwater concentrations are in Spencer *et al.* (1985). The active participation of pesticide manufacturers and growers should be solicited for this portion of the program.

IV. Reconnaissance of the Cache Creek watershed to determine the feasibility of mercury abatement programs Cache Creek drains a mercury rich watershed with several abandoned mercury mines (Montoya and Pan, 1992). Not known is whether these are the source of the mercury and what their relative contributions are. The mercury abatement program would monitor mercury concentrations periodically throughout the hydrologic cycle at key locations along the Creek to determine general locations in the watershed responsible for most of the loading. Follow-up work would focus on pin pointing sources in critical areas. Finally, an evaluation would be undertaken to determine the feasibility of initiating control programs at key locations.

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Table 1. Summary of diazinon concentrations (ppb) in surface water samples collected from the Central Valley and Delta.

location	time period	sample size	number of detections[4]	range[1]	number of samples exceeding[4] F&G[2]	Gammarid LC50[3]	reference
San Joaquin Valley	1988-90	15	12(80)	<0.1-1.59	12(80)	7(47)	Foe & Connor, 91b
Central Valley and Delta	winter 1992	40	26(65)	<0.1-6.84	26(65)	22(55)	Foe & Sheipline, 93
San Joaquin Valley	1991-92	272	178(65)	<0.01-2.60	84(31)	31(11)	Foe, 1995
San Joaquin River	1991-94	628	302(48)	<0.031-0.714	144(23)	30(5)	MacCoy *et al*. 1995
Sacramento River	1991-94	531	134(25)	<0.008-0.393	60(11)	5(1)	MacCoy *et al*. 1995
San Joaquin Valley	1991-93	317	100(32)	<0.050-36.0	100(32)	28(9)	Ross, 91;92a,b;93a,b,c

[1]Lower number indicates detection limit. [2]Fish and Game recommended chronic hazard assessment criteria of 0.040 ppb (Menconi and Cox, 1994). [3] Reported *Gammarus fasciatus* LC_{50} concentration of 0.2 ppb (Johnson and Finley, 1980). [4] Value(percentage of all samples analyzed).

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Table 2. Reported toxicity of diazinon (ppb) to selected aquatic organisms. A more extensive list of diazinon toxicity data is contained in Sheipline (1995).

Organism	life stage	toxicity test type	concentration	Citation
<u>*FISH*</u>				
Pimephales promelas (fathead minnow)	juvenile	96hrLC_{50}	6800	Allison & Hermanutz 1977
	embryo	34 day	NOEC[1]=92 LOEC[2]=170	Surprenant, 1988
Lepomis macrochirus (bluegill)	juvenile	96hrLC_{50}	168	Johnson & Finley 1980
Oncorhynchus mykiss (rainbow trout)	juvenile	96hrLC_{50}	90	Johnson & Finley, 1980
Chasmichtus dolichognathus (goby)	not reported	96hrLC_{50}	16	Hirose *et al*., 1979
<u>*INSECTS*</u>				
Cloeon dipterum (mayfly)	larvae	48hrLC_{50}	7.8	Hashimoto & Nishiuchi, 1981
Chironomus tentens (midge)	larvae	96hrLC_{50}	0.03	Morgan, 1976
<u>*CRUSTACEANS*</u>				
Mysidopsis bahia (Mysid)	<48 hrs	96hrLC_{50} 28 day	4.82 NOEC=1.15 LOEC=3.27	Nimmo *et al*. 1980
Neomysis mercedis (oppossum shrimp)	<24 hrs	96hrLC_{50}	1.91, 1.17	Bailey *et al*. 1995
Ceriodaphnia dubia (cladoceran)	<24 hrs	96hrLC_{50} 7 day	0.47, 0.41 IC_{25}=0.12[3]	Bailey *et al*. 1995 Per. Com. Mount
Daphnia magna (cladoceran)	<24 hrs	96hrLC_{50}	0.21	Mitchell, 1985
Gammarus fasciatus (Amphipod)	adult	96hrLC_{50}	0.20	Johnson and Finley, 1980

[1]Highest concentration not causing a significant effect. [2]Lowest concentration causing a significant effect. [3]Concentration causing a 25% reduction in reproduction in 7 days.

Table 3. Summary of recommended diazinon criteria (ppb).

	not to exceed			
Type	Concentration	Duration	Frequency	Reference
Acute	0.08	1 hour	3 years	Menconi & Cox, 94
Chronic	0.04	4 days	3 years	
Maximum	0.009	never to exceed		National Academy of Sciences, 73
Maximum	0.008	never to exceed		Inter. Joint Commission, 75